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Programmatic Summary: Self-Regulating, Self-Pressurizing Tubules for Integrated Circulatory Systems

by P. J. Costanzo, P. T. Dirlam, J. A. Orlicki, G. Palmese, and E. D. Wetzel

ARL-MR-0717 **February 2009**

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14. ABSTRACT

In this Director's Research Initiative (DRI) effort, we have developed surface treatments with cleavable Diels-Alder bonds that allow for a transition between wetting and non-wetting conditions via a combination of thermal and chemical treatments. These treatments are applied internally to glass capillaries to demonstrate the applicability of the technique for regulating flow in synthetic vascular systems. This report is a programmatic summary and will be supplemented by a complete technical report as a future publication.

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circulatory, vascular, Diels-Alder, self-healing,

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1. Objective

The objective of this research effort is to demonstrate microcapillaries with engineered internal surface activities that induce regulated, pressurized flow of internal vascular fluids (figure 1). A multistep coating and thermal process will be developed that can be used to create tubules whose initial, highly wettable internal surface can be switched to a surface of low-wettability. This thermally triggered switch in surface activity will allow the tubules to be easily filled with vascular fluid, sealed, and then converted to a state that spontaneously forces the fluid out of the tubule into surrounding void zones. This technology will greatly improve the effectiveness and tailorability of vascular composites, which promise new capabilities for self-healing of material damage (*1*), thermal management through structural "perspiration," active color control, and self-cleaning or decontaminating surfaces.

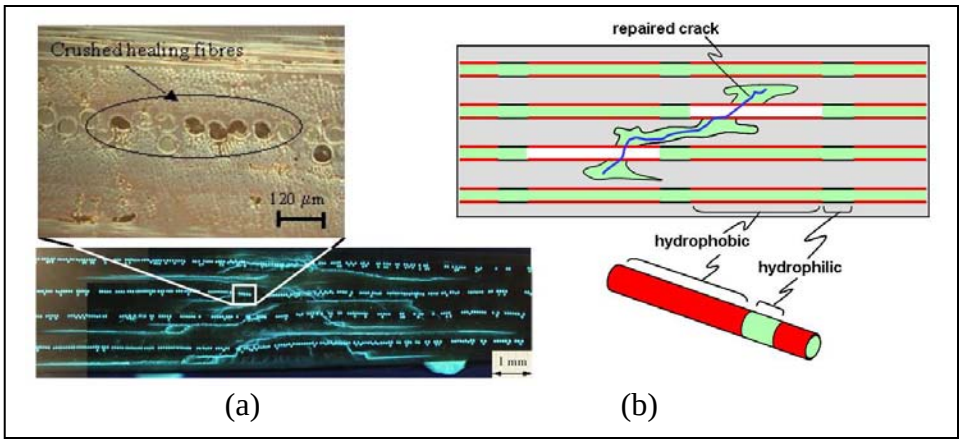

Figure 1. (a) A conventional vascular self-healing polymer (*1*) and (b) a concept for regulated self-pressurization through patterned surface properties.

2. Approach

2.1 Background

Many of the remarkable properties of biological systems are directly enabled by internal vascular networks. For example, our ability to heal and fight diseases relies on the ability to transport beneficial chemicals and specialized cells to and from damaged or diseased tissue. Warm-blooded animals regulate body temperature through perspiration, which requires transport of evaporative fluids to the outer surface of the skin. Plants transport nutrients and sugars between roots and leaves through vascular elements such as xylem and phloem in wood.

Recently, a number of researchers have demonstrated the ability to create vascularized structures, using techniques such as hollow glass capillaries (*1–3*) and direct-write fugitive inks (*4, 5*). These vascularized systems could impart many new functionalities to structural materials, such as active thermal management, self-healing, and mechanical property adaptation.

All of these applications require filling the vascular system with a vascular fluid, and moving this vascular fluid through the vascular channels. These tasks are most easily accomplished by coupling the vascularized system to an external mechanical pump. However, the weight, volume, complexity, and power requirements of most pumps drastically increase the complexity of the overall structure, and prevent the vascularized structure from providing standalone vascular capability.

An alternative approach is to actively control the surface energy of the vascular walls to modulate the wettability of the vascularized fluid. The internal vascular walls would be highly wettable during initial filling of the system, so that fluid incorporation would take place spontaneously. If the surface energy could then be switched to a non-wetting configuration, internal pressure would develop to drive the fluid out of the structure. Careful tailoring of the location of wetting and non-wetting regions, combined with active control of fluid entrance and exit ports on the structure, would result in active flow control without the need for external hardware. This approach is analogous to controlled transport in plants, which use tailored surface tension and evaporation techniques, rather than a central pump (such as a heart), to transport vascular fluids.

The primary challenge in creating this self-pressurizing system is the development of surfaces with actively controllable surface energy. One approach is using Diels-Alder chemistry. In a traditional Diels-Alder reaction, a diene is attacked by a dienophile resulting in a ring structure (figure 2). Ring formation is temperature dependent and therefore can be repeatedly reversed through heating and cooling the system. Incorporating these reversible bonds into functional surface chemistries should enable the creation of tailorable, reversible surface energies.

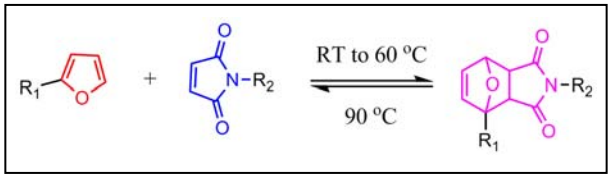

Figure 2. Reversible Diels-Alder adduct (purple), whose formation is temperature dependent; the red element is a diene, furan, and the blue element is a dienophile, maleimide.

This report summarizes our efforts to explore this self-pressurizing vasculature concept. We combined Diels-Alder chemistries with a range of functional groups to develop and demonstrate tailorable surfaces. Initial screening studies characterize the surface characteristics of coatings on flat glass substrates. We then applied the best coatings internally to glass capillaries. We also

present theoretical predictions of system performance. Complete details on the modeling and experimental work can be found in reference 6.

2.2 Experimental

Figure 3 displays the synthetic method employed to functionalize glass surfaces. The key aspect in the preparation of the thermo-responsive slide was the incorporation of a Diels-Alder linkage, where either a diene or dienophile is bound to the surface and the complimentary functional group is incorporated via a small molecule. All materials were purchased from commercially available sources and used as received. Standard characterization techniques were employed.

We prepared a Diels-Alder surface by silanizing with (3-aminopropyl)trimethoxy silane. Next, we treated the amino-terminated slides with a solution of 2-furoyl chloride to yield furan functionalized slides, which would act as a diene in a Diels-Alder reaction (*Surface 1*).

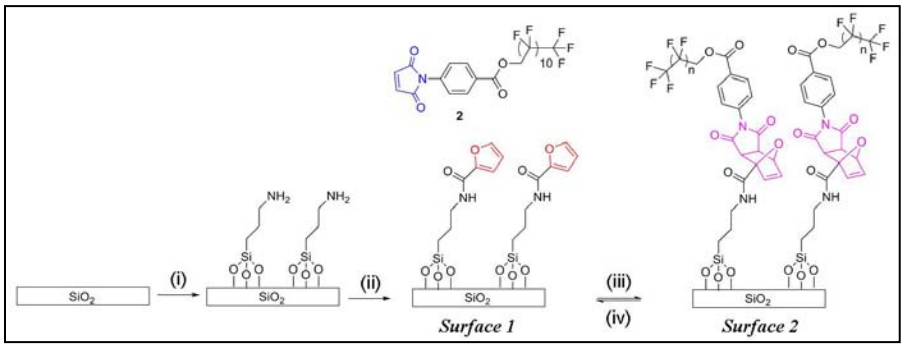

Figure 3. Synthetic route for preparation of functionalized glass slides. Conditions: (i) 3-aminopropyl silane; (ii) 2-furoyl chloride, Et_3N, CH_2Cl_2, 0 °C to RT, 24 h; (iii) Compound 2, THF, RT, 24 h.; and (iv) Toluene, reflux, 24 h.

Separately, we prepared a carboxy-maleimide according to previously reported methods (*7*) and functionalized it using esterification with 1H,1H-perfluoro-1-dodecanol to yield a hydrophobic dienophile component. Simply exposing the complementary functional groups to each other resulted in a Diels-Alder linkage and a hydrophobic surface (*Surface 2*). Thermal treatment cleaved the Diels-Alder linkage and restored the initial hydrophilic surface (*Surface 1*).

Next we explored a wide variety of Diels-Alder combinations. For example, we attached different maleimides to surfaces and prepared fluorinated furan agents. Ultimately, we chose the fluorinated furan route because of simplicity, overall yield, and ultimate contact angle change. Additional information, including synthetic procedures will be published elsewhere (*6*).

3. Results

3.1 Analytical Model of Self-pressurized Capillary

Consider the system shown in figure 4. A cylindrical capillary of diameter, D, and length, L, is filled with a fluid of viscosity, μ, with surface tension, γ. We define a capillary aspect ratio of $\lambda = L / D$. The fluid-wall contact angle is θ. At time $t = 0$, the fluid-air interface is located at position $x = 0$. The capillary is assumed to be horizontal, such that gravity effects can be neglected.

$$x(t) = \lambda D\left(1 - \sqrt{1 - \frac{t}{\alpha}}\right) \qquad v(t) = \frac{\lambda D}{2\alpha}\left(1 - \frac{t}{\alpha}\right)^{-\frac{1}{2}} \tag{1}$$

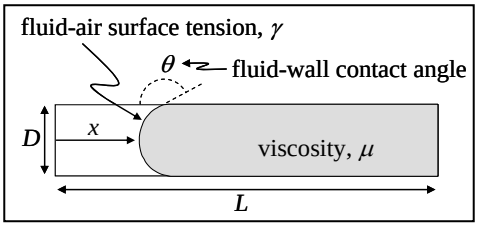

Figure 4. Analytical model parameter definition.

The position and velocity of the fluid interface as a function of time are given by reference 6.

The characteristic purge time, α, equal to the time required for the capillary to empty is given by

$$\alpha = \frac{4\mu L^2}{D\gamma\cos(\pi - \theta)} \tag{2}$$

where ($\lambda D / 2 \alpha$) is the initial interface velocity. The interface velocity increases with time and position, approaching infinite velocity at the capillary exit (when there are no viscous forces balancing capillary forces).

For water at room temperature, $\gamma = 0.07$ N/m and $\mu = 10^{-3}$ Pa s. Using these values and equation 2, figure 5a shows purge time (α) as a function of capillary aspect ratio and diameter, for the case of a water-filled capillary and a perfectly non-wetting fluid ($\theta = 180°$). Purge time increases with increasing aspect ratio and capillary diameter. Note that, even for large ($D = 1$ mm) capillaries with high aspect ratios ($\lambda = 1000$), the purge times are reasonable (10–100 s).

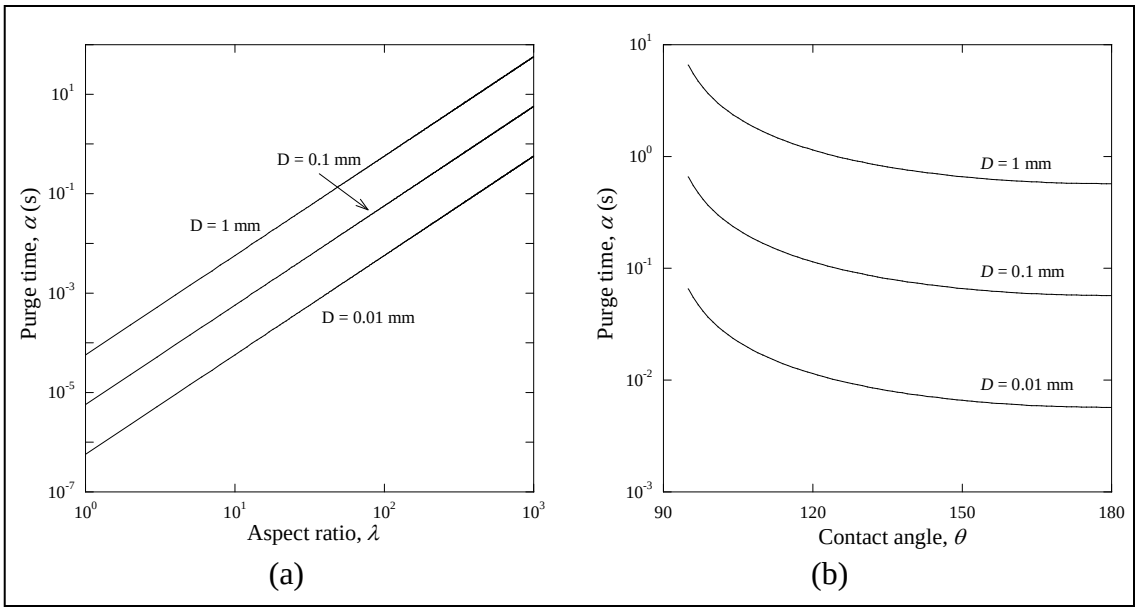

Figure 5. (a) Purge time as a function of capillary aspect ratio and diameter, for a water-filled capillary with a perfectly non-wetting contact angle and (b) purge time as a function of contact angle and capillary diameter, for a water-filled capillary with an aspect ratio of 100.

Figure 5b shows purge time as a function of contact angle, for different capillary diameters. Purge time decreases as capillary diameter decreases and contact angle increases. As the contact angle approaches 90° (neutrally wetting), there is no driving force for purging and the purge time becomes infinite. Note that decreasing contact angle from 180°– 95° results in only ca. one order of magnitude increase in purge time, regardless of capillary diameter.

3.2 Experimental Results

Table 1 displays contact angle measurements of glass slides during each stage of the functionalization, illustrating the clear change in surface energy due to surface composition. Figure 6 displays optical micrographs of contact angle experiments for *Surface 1* and *Surface 2*, demonstrating the significant change in contact angle due to surface functionalization.

Table 1. Contact angle measurements of glass slides at various stages of functionalization and the corresponding functionalized glass capillaries in figure 0.

Untreated (capillary A)	**APS** (capillary B)	**Furan** (capillary C) (*Surface 1*)	**Fluorinated** (capillary D) (*Surface 2*)	**Cleaved** (capillary E) (*Surface 1*)
23 ± 3 °C	58 ± 3 °C	70 ± 3 °C	101 ± 9 °C	70 ± 6 °C

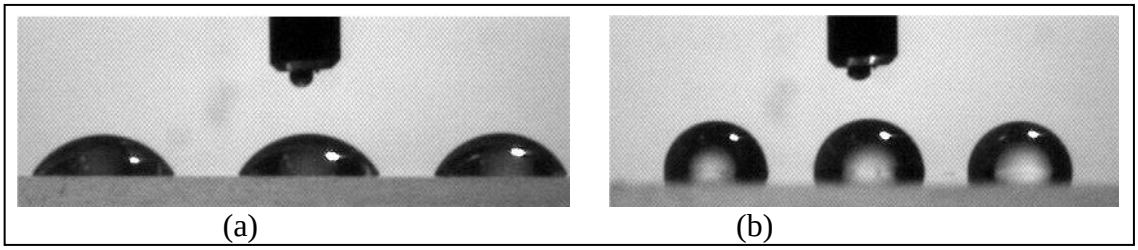

Figure 6. Contact angle measurements of (a) a furan functionalized slide (*Surface 1*) and (b) a fluorinated functionalized slide (*Surface 2*).

After successfully demonstrating the ability to alter surface energy on glass slides, the process was transitioned to glass capillaries with 1 mm inner diameter. Figure 7 displays capillaries at various stages of functionalization. Each surface chemistry provides a distinct and dramatic effect on capillary action within the tubes, with *Surface 1* chemistries showing high wettability and *Surface 2* showing low wettability.

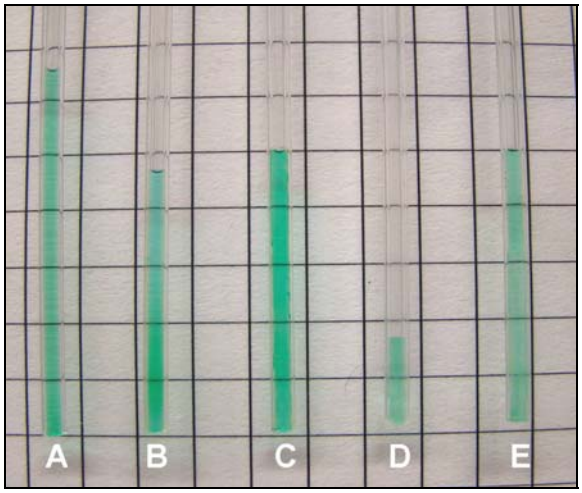

Figure 7. Optical micrographs of capillaries filled with dyed H_2O at various stages of functionalization, as described in table 1.

4. Conclusions

We completed theoretical modeling to illustrate how surface functionalization can affect surface energy, and ultimately, capillary action. We developed a thermo-responsive surface using Diels-Alder chemistry and modified surfaces following a simple, step-wise procedure that is straightforward and scalable. We then evaluated surfaces in hydrophilic and hydrophobic states, and demonstrated the ability to change surface energy. Overall, the technology was shown to be applicable to flat and curved surfaces.

Future work will investigate in-situ surface modification as well as flow experiments to determine expulsion times and efficiencies. Smaller capillaries will be used to limit the effect of gravitational forces, which prevented complete fluid expulsion in the current experiments (*6*). We will also explore patterning of surfaces to prepare vascular networks that are able to self-pressurize. Additionally, the current chemistry demonstrates a cleaving transition from hydrophobic to hydrophilic states. Work is underway to develop coatings that can instead be transitioned from hydrophilic to hydrophobic, which should prove more useful for many of our envisioned applications. Finally, while the current chemistry is infinitely reversible in theory, in practice the cleaving step results in a complete loss of the functionalized dienophile from the system. Eventually we hope to demonstrate reversible surface functionalizations that are partially tethered to the underlying substrates, so that the surface chemistry can be repeatably cycled between functionalizations within a closed system.

5. References

1. Trask R. S.; Bond, I. P. *Smart Mat. Struct.* **2006**, *15* (3), 704–710.
2. Trask R. S.; Bond, I. P.; Williams G. J. Bioinspired self-healing of advanced composite structures using hollow glass fibres. *J. Roy. Soc. Interface* **2006**, *4*, 363–371.
3. Bond, I. P.; Pang, J.W.C. Bleeding composites - Damage detection and self-repair using a biomimetic approach. *Composites* **2005**, *36*, 183–188.
4. Therriault, D.; White, S. R.; Lewis, J. A.; Shepher, R. F. Fugitive inks for direct-write assembly of three-dimensional microvascular networks. *Adv. Materials* **2005**, *17*, 395–399.
5. Therriault, D.; White, S. R.; Lewis, J. A. Chaotic mixing in three-dimensional microvascular networks fabricated by direct-write assembly. *Nature Materials* **2003**, *2*, 265–271.
6. Costanzo, P. J.; Dirlam, P. T.; Orlicstki, J. A.; Wetzel, E. D. Self-regulating, self-pressurizing tubules for integrated circulatory systems; ARL Technical report; U.S. Army Research Laboratory: Aberdeen Proving Ground, MD, in preparation.
7. Park, J. O.; Jang, S. H. Synthesis and characterization of bismaleimides for epoxy resins. *J. Poly. Sci. A.* **1992**, *30*, 723–729.

6. Transitions

The complete technical results will be documented in a U.S. Army Research Laboratory (ARL) technical report (*6*). ARL has coordinated with the University of Illinois and Drexel University on efforts related to vascularized structures and will continue to work with these partners to demonstrate controlled surface wettability in their systems. These efforts will be leveraged with internal ARL vascular and biomimetic research to drive the technology towards Army applications such as thermal management and impact damage recovery.

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